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(54) Abstract Title
Gaskets

(57) A gasket comprising a sealing layer formed from a resilient material which comprises exfoliated vermiculite, and a polymeric binder. The layer also comprises an intumescent material arranged to expand at temperatures at which said binder degrades. The intumescent material can be partially exfoliated vermiculite or unexfoliated vermiculite that has been treated to lower its exfoliation temperature. The intumescent material forms up to 20% by weight of the layer. The polymeric binder is a hydrolysis-resistant polymer coupled to the vermiculite by a coupling agent, such as silane. The polymer is selected from nitrile butadiene rubbers, styrene butadiene rubbers, natural rubber, butyl rubber and ethylene propyldiene monomer.

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GASKETS

This invention is concerned with gask--s, in particular with gaskets having a sealing-enhanci layer which is based on exfoliated vermiculite.

Exfoliated vermiculite is a known heat esistant resilient material. Exfoliated vermicuiite is conventionally formed by expanding mineral vermiculite using gas, this material being referred to herein as "gas-exfoliated vermiculite". The gas may be thermally generated, in which case the product is called "thermally-exfoliated vermiculite" (TEV). TEV may be made by flash-heating mineral vermiculite to 750-1000°c, at which temperature the water (free and combined) in the ore vaporises rapidly and the steam generated forces apart the silicate sheets which form the raw material, so bringing about an expansion of 10-20 times perpendicular to the plane of the sheets. The granules formed have a chemical composition which (apart from the loss of water) is virtually identical to that of the raw material. Gas-exfoliated vermiculite may also be made by treating raw vermiculite with a liquid chemical, eg hydrogen peroxide, that penetrates between the silicate sheets and subsequently evolves a gas, eg oxygen, to bring about exfoliation. A different form of exfoliated vermiculite is known as "chemically-exfoliated vermiculite" (CEV) and is formed by treating the ore and swelling it in water. In one possible preparation method, the ore is treated with saturated sodium chloride solution to exchange magnesium ions for sodium ions, and then with n-butyl ammonium chloride to replace sodium ions with n-$C_4H_9NH_3$ ions. On washing with water swelling takes place. The swollen material is then subjected to high shear to produce an aqueous suspension of very fine (diameter below 50 microns) vermiculite particles.

It is known to utilise exfoliated vermiculite as a layer of a sheet gasket, eg an automotive head gasket, and for other purposes. For example, GB 2 193 953 B discloses forming sheet-like gaskets formed from particles of gas-exfoliated vermiculite. Because such particles do not cohere well, it is necessary to incorporate a binder in the layer. One possible binder is provided by fine particles of CEV. However, although exfoliated vermiculite has excellent heat resistance and a high degree of resilience, it has poor water resistance, making desirable the use of a polymeric binder instead or in addition to a CEV binder. However, many polymeric binders de-grade at high temperatures creating voids through which fluids can leak. Thus, if the gasket is exposed to such temperatures, the gasket may cease to function.

It is an object of the present invention to provide a gasket comprising a sealing layer based on exfoliated vermiculite, which layer comprises a polymeric binder, the layer providing improved sealing at temperatures at which the binder degrades.

The invention provides a gasket comprising a sealing layer formed from a resilient material which comprises exfoliated vermiculite, and a polymeric binder, wherein the layer also comprises an intumescent material selected so that it expands at temperatures at which said binder degrades.

In a gasket according to the invention, at temperatures which cause the binder to degrade, the intumescent material expands to at least partially fill the void left by the binder, thereby helping to maintain sealing.

Preferably, the intumescent material is unexfoliated vermiculite because, after exfoliation, it has good heat

resistance. Another possibility is to use partially unexfoliated vermiculite, ie vermiculite which has been exfoliated at a lower temperature than is required to fully exfoliate it. The unexfoliated or partially exfoliated vermiculite may be treated (by methods which are known per se) to reduce the temperature at which exfoliation occurs, eg the temperature can be reduced to as low as 160°c. Other possible intumescent materials include expandable graphite, sodium silicate, and perlite.

The intumescent material may form up to 50% by weight of the layer but up to 20% is preferred.

In order to improve water-resistance, the polymeric binder may be a hydrolysis-resistant polymer coupled to the vermiculite by a coupling agent. For example, said polymer may be selected from nitrile butadiene rubbers, styrene butadiene rubbers, natural rubber, butyl rubber, and ethylene propyldiene monomer. Diene-based polymers are suitable because they are flexible and hydrolysis-resistant. The coupling agent may be a silane, eg a vinyl functional silane such as triethoxy vinyl silane ($(CH_3CH_2O)_3SiCH=CH_2$).

The sealing layer may be mechanically bonded to a metal sheet or other core material of the gasket. The mechanical bonding may be by tangs projecting from the sheet into the layer. The sheet may be of stainless steel, carbon steel, or wire mesh.

The exfoliated vermiculite is, preferably, CEV, but, since CEV is a relatively expensive material compared with gas-exfoliated vermiculite, eg TEV, in a gasket according to the invention, the sealing layer may also comprise particles of gas-exfoliated vermiculite, eg the layer may comprise particles of gas-exfoliated vermiculite and particles of CEV. The gas-exfoliated vermiculite may be

milled to a particle size of less than 50 microns. Other possible additives include talc, and mica.

There now follow detailed descriptions of three illustrative examples according to the invention.

In the first illustrative example, a tanged stainless steel sheet was first prepared. This sheet was 100 microns in thickness. The sheet was tanged by perforating it with square holes, each hole being 1.5 mm square and the hole centre-spacing being 3 mm. Half the holes were perforated by passing a tool through the sheet in a first direction and the remaining half, which alternated with the first-mentioned half, were perforated by passing a tool through the sheet in the opposite direction. The edges of the holes, thus, formed tangs projecting from the sheet in opposite directions. The tangs projected by about 1 mm.

In the first illustrative example, 0.741 Kg of an aqueous slurry (15% solids) of CEV particles was obtained from Grace Construction Products (designation "Microlite HTS"). To this slurry was added 0.074 Kg of particles of spray-dried CEV having particle size about 45 microns obtained from Grace Construction Products and designated "Microlite Powder". To this, was added 0.166 Kg of Dupre Superfine TEV. To this was added 19 g unexfoliated vermiculite, ie intumescent vermiculite. This gave a paste having approximately 37% solids. To this paste was added 4 g of a coupling agent (a vinyl functional silane called "Silquest A-151" obtainable from OSi Specialities) and further mixing was carried out.

Next, a hydrolysis-resistant polymer/solvent mixture was prepared. This mixture was 50 g of solid nitrile butadiene rubber (Nippon Zeon N36C80), 250 g of toluene, and 3.1 g of a curing agent ("Dicup 40", dicumylperoxide). 111 g of this mixture was added to the above-mentioned

paste and mixing by stirring was carried out. This gave a paste with approximately 5% rubber content.

Next, the paste (including the polymer/ lvent mixture) was spread over one side of the meta sheet mentioned above. The sheet was then passed etween calendering rollers and was dried. Further paste as then spread over the other side of the metal sheet and the calendering and drying was repeated. The sheet was then pressed to densify the resilient material which formed layers approximately 0.75 mm thick on both sides of the metal. Then it was heated to 180°c to peroxide cure the rubber. The layers contained approximately 5% by weight of intumescent vermiculite.

The completed gasket of the first illustrative example had two sealing layers formed from a resilient material. The resilient material comprised particles of CEV bonded together, and coupled to the nitrile butadiene rubber by the silane. The material also comprised particles of intumescent unexfoliated vermiculite. The gasket was tested to determine its water resistance by boiling in water for 5 hours. The gasket retained its integrity. The gasket was also tested at 450°c (a temperature which would be expected to de-grade the rubber and allow leakage) and no leakage was observed.

In the second illustrative example, the first illustrative example was repeated except that the TEV added to the slurry was omitted and replaces by further unexfoliated vermiculite, ie 0.185 Kg of unexfoliated vermiculite was added. This gave layers in the gasket containing 48.6% by weight of intumescent unexfoliated vermiculite.

In the third illustrative example, the first illustrative example was repeated except that 0.181 Kg of

TEV was added (instead of 0.166 Kg) and 4 g of unexfoliated vermiculite was added (instead of 19 g). This gave layers containing 1.1% by weight of intumescent unexfoliated vermiculite.

CLAIMS

1 A gasket comprising a sealing layer formed from a resilient material which comprises exfoliated vermiculite, and a polymeric binder, wherein the layer also comprises an intumescent material selected so that it expands at temperatures at which said binder degrades.

2 A gasket according to claim 1, wherein the intumescent material is unexfoliated vermiculite.

3 A gasket according to claim 1, wherein the intumescent material is partially exfoliated vermiculite.

4 A gasket according to either one of claims 2 and 3, wherein the intumescent vermiculite has been treated to lower its exfoliation temperature.

5 A gasket according to any one of claims 1 to 4, wherein the intumescent material forms up to 20% by weight of the layer.

6 A gasket according to any one of claims 1 to 5, wherein the polymeric binder is a hydrolysis-resistant polymer coupled to the vermiculite by a coupling agent.

7 A gasket according to claim 6, wherein said polymer is selected from nitrile butadiene rubbers, styrene butadiene rubbers, natural rubber, butyl rubber, and ethylene propyldiene monomer.

8 A gasket according to either one of claims 6 and 7, wherein the coupling agent is a silane.

9 A gasket according to any one of claims 1 to 8, wherein said sealing layer is mechanically bonded to a metal sheet of the gasket.

10 A gasket substantially as hereinbefore described with reference to the illustrative example.

The Patent Office

9

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Claims searched: 1-10

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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): F2B

Int Cl (Ed.6): F16J 15/10,15/12

Other: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0,379,636 A1 T&N Technology Limited	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.